

(11) (A)-No. 1:177 313

(45) ISSUED 841106

(52) CLASS 99-80
C.R. CL. 99-82

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(51) INT. CL. A23F 3,38,5/22

(19) (CA) **CANADIAN PATENT** (12)

(54) Slurry Decaffeination

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(73) Granted to General Foods Corporation
U.S.A.

(21) APPLICATION No.	378,270
(22) FILED	810525
(30) PRIORITY DATE	U.S.A. (159,909) 800616

No. OF CLAIMS 25 - NO DRAWING

Canada

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DESCRIPTION

SLURRY DECAFFEINATION

Technical Field

05 The present invention relates to decaffeination,
and more particularly to a new process for de-
caffeinating an aqueous solution by contacting it
with a two phase extractant, namely a slurry of a
solid adsorbent in a liquid caffeine-specific solvent.

10 The prior art has long sought a process to
effectively and non-destructively remove caffeine
from aqueous solutions, such as vegetable extracts
from tea, coffee, and the like. All of the known
procedures have at least two common problems.
First, they add cost to the final product, and it
15 would be desirable to reduce that cost as much as
possible. Secondly, they all affect the flavor and
quality of the final product by either altering the
chemical profile of the natural ingredients or
possibly by leaving minor residues. Therefore, it
20 would be desirable to provide an alternative procedure
which is more economical than known technology for
producing products of like or improved flavor and
quality.

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Background Art

Commercial decaffeination techniques often involve solvent extraction from whole green beans such as described by Patel et al. in U.S. 3,671,263 who use a chlorinated hydrocarbon solvent, and by Berry et al. in U.S. 2,309,092 who use a caffeine-deficient solution of coffee solubles. Also of commercial importance is the extraction of caffeine from aqueous solutions with a water-immiscible solvent as described by Adler et al. in U.S. 2,933,395.

However, a wide variety of other processes have been described in the patent literature to enable the use of alternative solvents or eliminate the need for solvent/ product contact. For example, in Belgian Patent 835,556 there is disclosed a process wherein aqueous caffeine solutions are contacted with liquid, water-immiscible fatty extractants at ratios of liquid extractant to caffeine solution of about 20:1. The high volumes of extractant seriously detract from the commercial utility of such a process because of the high added costs.

In an alternative to the use of highly caffeine-specific solvents, Katz suggests in U.S. 4,113,886 that a selective membrane can be employed to effect separation. The solvent is used only to transfer the caffeine from the feed solution to an aqueous phase for collecting the extracted caffeine.

As a total alternative to liquid extractants, a number of patents teach solid adsorbents. For example, U.K. Patent 1,448,340 describes removing caffeine from an aqueous solution by means of polymeric non-ionogenic adsorption resins. While certain of these resins are effective and produce high quality products, they are more costly than desired. Other

patents, such as U.S. 2,391,981 and U.S. 2,416,484 to Kremers, discuss clay as an adsorbent, however, clay is not satisfactorily selective for commercial use as such. Similarly, the hydrated silicates as disclosed by Grossman in U.S. 2,375,550 remove valuable coffee solids other than caffeine. Other patents, such as U.S. 2,472,881 to Bender, U.S. 2,508,545 to Shuman, and U.S. 4,168,324 to Roselius et al, disclose the attraction of caffeine by activated carbon. However, none of these patents suggest decaffeination of an aqueous extract by direct contact with activated carbon because the activated carbon is not specific to caffeine and picks up many other solids.

Thus, the prior art attempts with liquid fatty extractants need improvement to reduce the large amounts of extractant required, and the systems employing solid adsorbents are either too costly or not selective enough. Accordingly, there is a present need for improvement and the provision of an alternative process for decaffeination.

Disclosure of Invention

The present invention provides a new method for decaffeinating an aqueous caffeine-containing solution comprising the steps of: (a) contacting an aqueous caffeine-containing solution with a slurry containing a solid caffeine adsorbent and a liquid, water-immiscible, caffeine-specific solvent; (b) maintaining the aqueous caffeine-containing solution in contact with the slurry for a time sufficient for at least a portion of the caffeine to be extracted from the aqueous solution and adsorbed by the solid caffeine adsorbent; and (c) separating the aqueous caffeine-containing solution from the slurry.

The process is useful for removing caffeine from any aqueous caffeine-containing solution, but finds its primary utility for decaffeinating aqueous vegetable extracts such as coffee and tea. Because
05 of its high specificity for caffeine, the coffee extracts can be from green or roasted beans. Where the extract is from roasted coffee, it is preferred to strip and collect volatile flavors and aromas from the aqueous extract before contacting the
10 extract with the slurry for removing the caffeine. Then, the decaffeinated extract can be combined with the collected volatiles and dried to soluble powder form as described in U.S. 2,933,395 to Adler et al. There are envisaged, however, products for which
15 this will not be necessary and alternative processes wherein the volatiles can be removed from the water-immiscible solvent employed in the slurry.

The liquid, water-immiscible caffeine-specific solvent employed in the extractant slurry provides
20 two principal functions. First, it extracts the caffeine from the aqueous feed solution; and secondly, its high selectivity for caffeine screens out other valuable materials present in the feed solution. An advantage of the invention is that the solvent need
25 not have a high capacity for holding caffeine. Therefore, solvents with high selectivity, but low capacities for holding caffeine can be employed with good effectiveness. The solvent is constantly cleaned of caffeine by the solid caffeine adsorbent.
30 Another advantage of the invention is that the selectivities of the solvent and the solid adsorbent are additive and the slurry is more selective than either would be separately.

Selection of the proper combination of solvent, solid adsorbent, ratio of solvent to adsorbent, and conditions of contact is important to maintain the most effective driving force and rate of decaffeination.

- 05 As a general guide, it is desirable to operate with suitable solvents and solid adsorbents in suitable relative amounts and at suitable conditions of time and temperature of contact, to maintain the concentration of caffeine in the solvent at levels
10 of less than 0.03% based on the weight of the solvent. Preferably, the caffeine concentration will be maintained at a concentration of less than 0.015%. Ultimately, economics must dictate this value, and concentrations outside of these limits may be
15 preferred in some situations.

- The solvent must be a liquid under the proposed processing conditions and must be immiscible in the aqueous caffeine-containing feed solution. It is important for the solvent to be liquid so that
20 liquid-liquid contact with the feed solution can be established. Preferably, the viscosity of the solvent will be sufficiently low that the level of mixing shear normally encountered in liquid-liquid extraction will keep it adequately dispersed within
25 the aqueous feed solution. The quality of immiscibility is important so that the solvent is not dissolved in the aqueous caffeine-containing solution in any amount which will have a significant impact on the flavor or quality of the final product. Preferably,
30 the solvent is sufficiently immiscible to prevent any measurable amount of it to be dissolved in the aqueous caffeine-containing solution. Also, it is important for the solvent and the solid adsorbent to be mutually attracted sufficiently to maintain the

solid adsorbent in the solvent phase and out of aqueous phase.

Among the materials which can be employed as solvents according to the present invention are
05 petroleum oils, triglycerides, fatty acids, fatty alcohols and other caffeine-specific, water-immiscible materials which are liquid at the conditions of treatment. The triglycerides can be derived from vegetable or animal sources. Among the
10 suitable triglycerides are the usual vegetable fats typically encountered in food processing, such as soybean oil, corn oil, coconut oil, cottonseed oil, peanut oil, safflower oil, palm kernel oil, sunflower oil, palm oil, rapeseed oil, coffee oil, and
15 mixtures of these. Preferably the fat will be naturally low in emulsifying potential or will be treated such as by an initial emulsification in water under high shear conditions and separating out all portions which do not readily recombine with
20 the major portion of the oil. It is also preferred that the caffeine-specific solvent have a partition coefficient above 0.02, and more preferably above 0.1.

While hydrogenated fats can be employed, they
25 are not preferred because they may smoke and break down under the high temperatures employed in processing, especially those encountered during periodic purification of the oil. Similarly, animal fats such as tallow, chicken fat, lard and butter fat can
30 conceivably be employed, but they contain large amounts of impurities which are costly to remove. However, economics is the primary reason for their non-preference. Among the suitable petroleum oils are mineral oils known to the art as light mineral

oils. These oils are desirable because they have good stability. Among the fatty acids are oleic acid, stearic acid, octanoic acid, and the like. In general, the longer chain acids will be preferred within this group. Similarly, longer chain fatty alcohols, such as stearyl alcohol, are preferred within that group.

The solid caffeine adsorbent employed in the slurry of the present invention can be selected from any of those known to adsorb caffeine and be physically stable under the conditions of processing. Among the known caffeine adsorbents are clays such as discussed in U.S. 2,391,981 and U.S. 2,416,484 to Kremers; zeolites and ion exchange resins as taught in U.S. 3,108,876 to Turken et al; hydrated silicates as taught in U.S. 2,375,550 to Grossman; polymeric non-ionogenic adsorption resins, especially styrene divinylbenzene macroreticular resins of the type disclosed by Gustafson in U.S. 3,531,463; activated carbon, especially finely-divided activated carbon derived from coconut or coal. Among these, activated carbon is preferred because of its desirable balance between cost and effectiveness.

The solid adsorbent should have the highest possible surface area consistent with physical strength necessary under the processing conditions and the facility with which it can be separated from the water-immiscible solvent after contacting the slurry with the aqueous caffeine-containing solution for the desired period of time. In the case of activated charcoal, especially derived from coconut or coal, particle sizes of from 100 to 300 U.S. mesh have been found effective. The natural porosity of these materials further increases their surface area

and increases the efficiency with which they remove caffeine from the solvent.

05 The concentration of the solid adsorbent in the water-immiscible solvent will depend upon a number of factors including: the concentration of caffeine in the aqueous feed solution, the combined capacity of the solid adsorbent and the liquid solvent to hold caffeine, the individual capacity of the solvent to hold caffeine and yet maintain a high driving
10 force to continue extraction, the individual capacity of the solid adsorbent to hold caffeine and yet maintain a high driving force to continue removing the caffeine from the solvent, the desired reduction in caffeine concentration in the aqueous feed solution,
15 the rate at which the solid adsorbent is renewed in continuous processing, the available quantities of slurry for contacting with the aqueous liquid, and various other factors, including economics, which can affect or control any of the listed factors.

20 Not all of these factors and their interrelationships have been studied in detail, however, it appears desirable to maintain the combined capacity of the solvent and the adsorbent at a level at least equal to the total amount of caffeine in the system.
25 And, the solid adsorbent should be present in an amount effective to provide a capacity to hold at least half of that total caffeine. Preferably, the combined capacity should be at least 50% greater than the amount of caffeine in the solution in
30 contact with the slurry. Preferably, the slurry will contain from about 2 to about 50% solid adsorbent based on the weight of the slurry. Most preferably, the slurry will comprise from about 5 to 20% of the

solid caffeine adsorbent, based on the weight of the slurry.

05 An advantage of the present invention is the reduced level of solvent required as compared to prior art processes employing water-immiscible fatty materials as solvents. Ratios of the weight of slurry to the weight of aqueous caffeine-containing solution can be considerably less than 20:1 and ratios of 1:1 and lower can be used with some 10 effectiveness. More preferred ratios are within the range of from about 2:1 to about 10:1. It is most preferred to maintain the ratio of the weight of the solvent to the weight of the solution to less than 5:1, and this can be achieved with facility according 15 to the invention where the amount of solid adsorbent added to the solvent to form the slurry is effective to maintain the concentration of caffeine in the solvent at a level of less than 0.03%, based on the weight of the solvent. Where the adsorbent is 20 activated carbon, and the aqueous caffeine-containing solution is a typical coffee extract containing from about 10 to about 35%, and most typically from 15 to 28%, solids including caffeine, carbon concentrations of from about 5 to about 20% of the weight of the 25 slurry will be effective.

The process of this invention can be employed to obtain any desired degree of caffeine removal. The process is adaptable to batch, semi-continuous and continuous processing with concurrent or counter- 30 current flow. Preferably, however, it is performed continuously by countercurrently passing the slurry and a caffeine-rich aqueous solution into a liquid-liquid contactor such as a rotating disc contactor or a Karr column. The slurry and the aqueous solution

are easily separated due to their requisite immiscibility. The slurry is then continuously filtered to remove the adsorbent and fresh activated carbon is continuously added prior to recycling the solvent to the liquid-liquid contactor. The carbon can be renewed by known processes such as heating and solvent regeneration.

The oil remains relatively clean and needs no treatment to remain effective. However, over a period of time, the oil may degrade or be filled with other undesirable components and can be discarded or renewed according to known techniques. For example, it can be heated to sublime the caffeine. It is an advantage of the present invention, however, that the solvent does not need to be specially processed simply to remove the caffeine to maintain a high driving force for the extraction. The solid caffeine adsorbent continuously removes excess caffeine levels from the solvent to maintain a good extraction rate.

Also important for obtaining good extraction according to the invention is the temperature maintained during contact between the slurry and the aqueous caffeine solution. The temperature will affect the rate of extraction, the selectivity of the solvent, and the relative capacities of the slurry components for holding the extracted caffeine. The temperature will also affect the flavor of any desired coffee or tea flavors present in the aqueous solution. Accordingly, it is not possible to identify a single temperature or range of temperatures as universally defining optimum conditions. It is believed, however, that temperatures within the range of from about 50 to about 100°C will provide good results. The selection

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of an exact temperature will depend on the materials and processing equipment and conditions employed, and may be within this range or outside of this range.

- 05 Total contact time, or residence time within a liquid-liquid contactor, will depend upon the factors discussed above as well as the desired degree of caffeine extraction. While economics is the controlling factor, it must be borne in mind that excessively
10 long contact times adversely affect coffee and tea flavors. Those skilled in the art will be able to balance these factors as necessary, given the exemplary situations set forth in the Example.

Best Mode For Carrying Out The Invention

- 15 The following Example is provided to illustrate and explain what is presently considered the best mode for carrying out the invention. The data is for illustrative purposes to guide the person of ordinary skill in the art and is not to be taken as
20 limiting in any regard. Unless otherwise indicated, all parts and percentages are by weight.

Example

- 25 A series of green and roasted coffee extracts were decaffeinated by contacting them with slurries containing the indicated water-immiscible solvents and 10%, by weight of the slurry of DARCO* 51 fine activated carbon.

- 30 The green coffee extracts had total solids contents of 25% and a ratio of total solids to caffeine of 25.2.

 The roasted coffee extracts had total solids contents of 20% and a ratio of total solids to caffeine of 20.8.

* Trade Mark

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05 All extractions were done in batches of 0.1 kilograms total weight for 20 hours at 82°C. Each extraction employed 0.02 kg aqueous coffee extract and 0.08 kg of the indicated solvent and carbon for a solvent to extract ratio of 4:1. The results are summarized in the table below and show good decaffeination and good specificity.

10	<u>Extract</u>	<u>Solvent</u>	Percent Decaffeina- <u>tion</u>	Product Ratio of	Apparent	Solid
				Total Solid/ Caf- <u>feine</u>	Process Partition Coef- <u>ficient</u>	Adsorbent Partition Coef- <u>ficient</u>
15	Green	Mineral Oil	38.0	40.5	0.15	1.53
	Green	Corn Oil	49.4	49.7	0.24	2.44
	Roasted	Mineral Oil	52.8	44.1	0.28	2.80
	Roasted	Corn Oil	50.3	41.9	0.25	2.53

20 The above description is for the purpose of describing the invention to people having ordinary skill in the art to enable them to practice it. It is not meant to detail all of the obvious modifications and variations of the invention which will become apparent upon reading. It is intended, however,
25 that these modifications and variations be included within the scope of the invention which is defined by the following claims.

CLAIMS

1. A method for decaffeinating an aqueous caffeine-containing solution comprising the steps of:
 - 05 (a) contacting an aqueous caffeine-containing solution with a slurry containing a solid caffeine adsorbent and a liquid, water-immiscible, caffeine-specific solvent;
 - 10 (b) maintaining the aqueous caffeine-containing solution in contact with the slurry for a time sufficient for at least a portion of the caffeine to be extracted from the aqueous solution and adsorbed by the solid caffeine adsorbent; and
 - 15 (c) separating the aqueous caffeine-containing solution from the slurry.
2. The method of claim 1 wherein the aqueous caffeine-containing solution is a coffee or tea extract.
3. The method of claim 2 wherein the aqueous
20 caffeine-containing solution is a green coffee extract.
4. The method of claim 2 wherein the aqueous caffeine-containing solution is a roasted coffee extract.
- 25 5. The method of claim 4 wherein the roasted coffee extract has been stripped of volatiles.
6. The method of claim 1 wherein the solid adsorbent is continuously removed from the slurry and renewed adsorbent is continuously added.
- 30 7. The method of claim 6 wherein the temperature during contact is maintained within the range of from 50° to 100° C.
8. The method of claim 1 wherein the solid caffeine adsorbent comprises a member selected from the group

consisting of activated carbon, clay, hydrated silicates, zeolites, ion exchange resins, non-ionogenic adsorption resins, and any combination of these.

- 05 9. The method of claim 8 wherein the solid caffeine adsorbent comprises activated carbon.
- 10 10. The method of claim 1 wherein the liquid, water-immiscible, caffeine-specific solvent comprises a member selected from the group consisting of petroleum oils, fatty acids, fatty alcohols, and triglycerides.
11. The method of claim 1 wherein the slurry comprises from 2 to 50% solid caffeine adsorbent based on the weight of the slurry.
- 15 12. The method according to any one of claims 9, 10 or 11 wherein the slurry comprises from 5 to 20% solid caffeine adsorbent based on the weight of the slurry.
- 20 13. The method according to claim 1 wherein the ratio of weight of the slurry to the weight of the aqueous caffeine-containing solution is within the range of from 1:1 to 20:1.
- 25 14. The method according to any one of claims 9, 10, or 11 wherein the ratio of the weight of the slurry to the weight of the aqueous caffeine-containing solution is within the range of from 2:1 to 10:1.
- 30 15. The method of claim 1 wherein the concentration of caffeine in the liquid, water-immiscible, caffeine-specific solvent is maintained at less than 0.03% based on the weight of the solvent.
16. The method of claim 1 which further comprises the step of separating the liquid, water-immiscible, caffeine-specific solvent from the solid caffeine adsorbent.

17. The method of claim 16 which further includes the step of removing the caffeine from the solid caffeine adsorbent.
- 05 18. The method of claim 16 which further includes the step of removing the caffeine from the liquid, water-immiscible, caffeine-specific solvent.
- 10 19. The method according to claim 16 wherein concentration of caffeine in the liquid, water-immiscible, caffeine-specific solvent is maintained at a less than 0.03% based on the weight of the solvent.
- 15 20. The method according to claim 16 wherein the liquid, water-immiscible, caffeine-specific solvent comprises a member selected from the group consisting of petroleum oils, fatty acids, fatty alcohols, and triglycerides.
- 20 21. The method according to claim 20 wherein the solid caffeine adsorbent comprises activated carbon.
22. The method according to claim 21 wherein the ratio of the weight of the slurry to the weight of the aqueous caffeine-containing solution is within the range of from 2:1 to 10:1.
- 25 23. The method according to claim 22 wherein the slurry comprises from 5 to 20% activated carbon based on the weight of the slurry.
24. The method according to claim 23 wherein the temperature during contact is maintained within the range of from 50° to 100° C.
- 30 25. The method of claim 24 wherein the ratio of liquid, water-immiscible, caffeine-specific solvent to aqueous caffeine-containing solution is less than 5:1.



SLURRY DECAFFEINATION

ABSTRACT

05 The object of the invention is to provide an improved method for removing caffeine from aqueous solutions such as coffee and tea extracts.

10 Decaffeination with water-immiscible fatty materials is impractical because the ratio of fatty material to aqueous caffeine solution will typically be about 20:1. Non-solvent systems employing solid adsorbents have not been commercially practical because they are either too non-selective or too expensive.

15 The process disclosed herein decaffeinate an aqueous caffeine solution by contacting it with a slurry comprising a solid caffeine adsorbent and a water-immiscible, caffeine-specific solvent. The caffeine is selectively extracted from the aqueous solution, leaving the solubles necessary for a good tasting beverage, and then removed from solution by
20 the solid adsorbent. Because the solvent is selective, the adsorbent does not have to be. And, because the adsorbent continuously maintains a low concentration of caffeine in the solvent, much lower solvent to aqueous solution ratios can be employed, preferably
25 less than 5:1.